

CH 222: Lectures and Labs

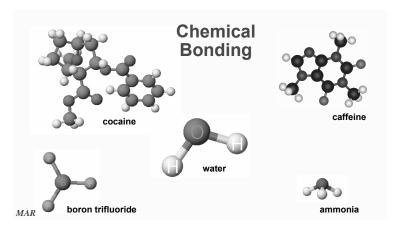
Lectures: MWF from 9 - 9:50 AM in AC 1303 (this room)

- Lectures recorded, available soon afterwards
- Lecture notes to print available (under "Problem Sets and Handouts", mhchem.org/222), get CH 222 Companion as soon as possible

Labs (Section 01): Mondays from 1:10 - 5 PM

- Start in room AC 2501 (not AC 1303)
- Move to AC 2507 ("the lab") around 3 PM
- For first day, bring a printed copy of the "Chromatography" Lab (mhchem.org/222), a pair of safety glasses (Dollar store ok) and your calculator

MAR ...more on Monday afternoon



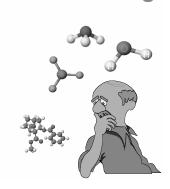
Chemical Bonding

Problems and questions:

How is a molecule or polyatomic ion held together? Why are atoms distributed at strange angles? Why are molecules not flat? Can we predict the structure? How is structure related to chemical and physical

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properties?



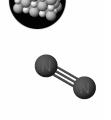
Two Extreme Forms of Chemical Bonds

IONIC - complete transfer of electrons from one atom to another, metals + nonmetals

Covalent - electrons shared between atoms, mostly nonmetals

Most bonds are somewhere in between

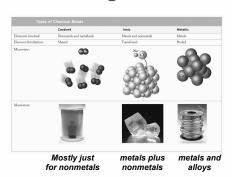
Also Metallic - for metals, studied later



December 2018: Metavalent bonding (for metalloids!)

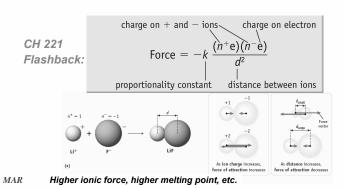
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Bonding Overview



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Ionic Forces - Coulomb's Law



Covalent Bonding Covalent bonds arise from the mutual attraction of 2 nuclei for the same electrons. Attractive Electron cloud Repulsive Nucleus A covalent bond is a balance of attractive Interatomic Interactions and repulsive forces.

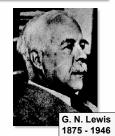
Covalent Bonding

Covalent bonding will be the focus of the first two chapters We will re-visit lonic bonding and Metallic bonding in a future chapter Important to know when a compound is ionic, covalent or metallic!





Electron Distribution in Molecules



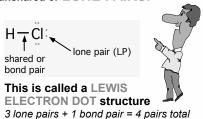
Electron distribution is depicted with Lewis electron dot structures

Valence electrons are distributed as shared or BOND PAIRS and unshared or LONE PAIRS.

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Bond and Lone Pairs

Valence electrons are distributed as shared or BOND PAIRS and unshared or LONE PAIRS.



Bond Formation

A bond can result from a "head-tohead" OVERIAD of atomic orbitals on neighboring atoms, making a sigma (σ) bond.



Overlap of H (1s) and Cl (3p)

Note that each atom has a single, unpaired electron in their atomic orbital.

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Valence Electrons

Electrons are divided between COTE and

valence electrons

B 1s² 2s² 2p¹

Core = [He], valence = 2s² 2p¹ 2 core e⁻, 3 valence e⁻



Br [Ar] 3d¹⁰ 4s² 4p⁵ Core = [Ar] 3d¹⁰, valence = 4s² 4p⁵ 28 core e⁻, 7 valence e⁻



88 **Valence Electrons** 1A 2 He Н٠ 2A 4A 5A 6A 7A Be ·B :0 .. Number of valence electrons is equal to the Group number

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Building Lewis Structures

No. of valence electrons of a main group atom = Group number

For Groups 1A - 4A, no. of bond pairs = group number.

For Groups 5A - 7A, BPs = 8 - Grp. No.







Building a Lewis Dot Structure

No. of valence electrons of an atom = Group number

For Groups 1A - 4A (14), no. of bond pairs = group number

For Groups 5A (15) - 7A (17), BPs = 8 - Grp. No.

Except for H (and sometimes atoms of 3rd and higher periods),

$$BPs + LPs = 4$$

This observation is called the

OCTET RULE



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Building a Lewis Dot Structure

Ammonia, NH₃

1. Count valence electrons

H = 1 and N = 5Total = $(3 \times 1) + 5$

= 8 electrons or

4 pairs of electrons

2. Decide on the central atom; never H.

Central atom is atom of lowest affinity for electrons.

Therefore, N is central

Building a Lewis Dot Structure

3. Form a sigma bond (single bond) between the central atom and surrounding atoms.

H—N—H | |

 Remaining electrons form LONE PAIRS to complete octet as needed.



3 BOND PAIRS and 1 LONE PAIR. Note that N has a share in 4 pairs (8 electrons), while H shares 1 pair.

ndout

Unshared electron pairs ("lone pairs") take up more volume than shared electron pairs ("bonding pairs")

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MAR See <u>Building Lewis Structures</u> handout

Sulfite ion, SO₃²-

Step 1. Central atom = S

Step 2. Count valence electrons

S = 6

 $3 \times 0 = 3 \times 6 = 18$

Negative charge = 2

TOTAL = 26 e- or 13 pairs

Step 3. Form sigma bonds

10 pairs of electrons are

now left.



Sulfite ion, SO₃²-

Remaining pairs become lone pairs, first on outside atoms and then on central



Each atom is surrounded by an octet of electrons.

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Carbon Dioxide, CO₂

- 1. Central atom = _
- 2. Valence electrons = __ or __ pairs
- 3. Form sigma bonds.

This leaves 6 pairs.

4. Place lone pairs on outer atoms.

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Carbon Dioxide, CO₂

4. Place lone pairs on outer atoms.

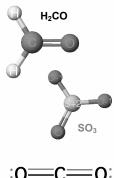
5. So that C has an octet, we shall form DOUBLE BONDS between C and O.

$$: \ddot{\mathbb{Q}}_{\bullet}^{-C} - \ddot{\mathbb{Q}} \ddot{\mathbb{Q}} : \longrightarrow : \ddot{\mathbb{Q}} = C = \ddot{\mathbb{Q}} :$$

The second bonding pair forms a $pi(\pi)$ bond.

Double and even triple bonds are commonly observed for C, N, P, O, and S





Sulfur Dioxide, SO₂

- 1. Central atom = S
- 2. Valence electrons = 18 or 9 pairs

3. Form pi (π) bond so that S has an octet - but note that there are two ways of doing this.

> bring in OR bring in left pair right pair

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Sulfur Dioxide, SO₂

This leads to the following structures.

These equivalent structures are called RESONANCE STRUCTURES. The true electronic structure is a HYBRID of the two.

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Violations of the Octet Rule

Usually occurs with B and elements of higher periods.





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Boron Trifluoride

Central atom =

Valence electrons =

or electron pairs =

Assemble dot structure



The B atom has a share in only 6 electrons (or 3 pairs). B atom in many molecules is electron deficient.

Also common for Al and Be

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Sulfur Tetrafluoride, SF₄

Central atom =

Valence electrons = ___ or ___ pairs.

Form sigma bonds and distribute electron pairs.

:Ë — S — E : :Ë — F :

5 pairs around the S atom. A common occurrence outside the 2nd period.

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Odd # of electrons: NO₂

Paramagnetic compounds & free radicals

For NO₂, central atom = ____

Valence electrons = ___ or ___ pairs.
Odd e- occupies its own "space"

Form sigma bonds and distribute electron pairs.

$$\stackrel{: \ddot{O}}{\longrightarrow} \stackrel{: \ddot{O}}{\longleftarrow} \stackrel{: \ddot{O}}{\longleftarrow} \stackrel{: \ddot{O}}{\longrightarrow} \stackrel{:$$

Paramagnetic
materials are attracted by a strong magnet.

Diamagnetic
materials are repelled by a strong magnet.

Paramagnetic substances often more reactive than diamagnetic substances

Formal Atom Charges

Atoms in molecules often bear a charge (+ or -).

The predominant resonance structure of a molecule is the one with charges as close to 0 as possible.

Formal charge = Group number - $\frac{1}{2}$ (number bonding electrons) - (number lone pair electrons (lpe)),

FC = GN - bonds - lpe

Sum of all formal charges in a molecule must equal ionic charge

See Guide to Formal Charges

Formal Atom Charges

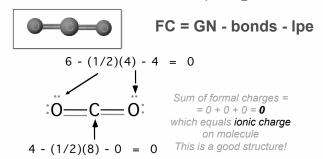
Formal charge = Group number - $\frac{1}{2}$ (number bonding electrons) - (number lone pair electrons)

FC = GN - bonds - Ipe

Formal Charges In Isomers

more stable structure -c**≡**n: N≡C:

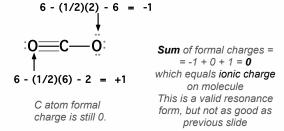
Carbon Dioxide, CO₂



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Formal Charge Comparison with CO₂

FC = GN - bonds - Ipe

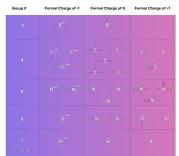


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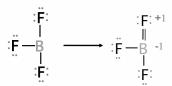
Formal Charge

FORMAL CHARGE = GROUP # - (BONDS + NONBONDING ELECTRONS)



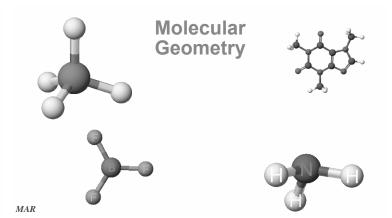
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Boron Trifluoride, BF₃



What if we form a B-F double bond to satisfy the B atom octet?

F never makes double bonds!



MOLECULAR GEOMETRY

VSEPR

Valence Shell Electron Pair Repulsion theory.

Most important factor in determining geometry is relative repulsion between electron pairs.



Molecule adopts the shape that minimizes the electron pair repulsions.

See Geometry and Polarity Guide

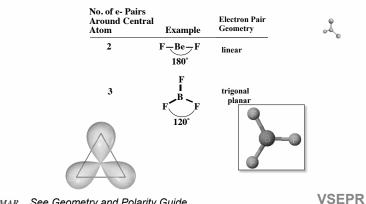
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No. of e- Pairs **Around Central** Example Geometry Atom 2 F-Be-F linear 180°

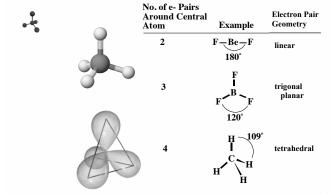


MAR See Geometry and Polarity Guide

VSEPR



MAR See Geometry and Polarity Guide



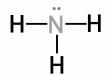
MAR See Geometry and Polarity Guide

VSEPR

Structure Determination by VSEPR

Ammonia, NH₃

- 1. Draw electron dot structure
- 2. Count BPs and LPs = 4
- 3. The 4 electron pairs are at the corners of a tetrahedron.





lone pair of electrons in tetrahedral position

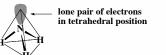
> The ELECTRON PAIR GEOMETRY is tetrahedral.

> > MAR

Structure Determination by VSEPR

Ammonia, NH₃

The electron pair geometry is tetrahedral.





The MOLECULAR GEOMETRY - the positions of the atoms - is TRIGONAL PYRAMID

See Geometry and Polarity Guide

Structure Determination by VSEPR

Water, H₂O

- 1. Draw electron dot structure
- 2. Count BPs and LPs = 4
- 3. The 4 electron pairs are at the corners of a tetrahedron.



The electron pair geometry is TETRAHEDRAL



Structure Determination by VSEPR

Water, H₂O H-Ö-H

The electron pair geometry is TETRAHEDRAL

The molecular geometry is bent



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Structure Determination by VSEPR

Methanol, CH₃OH

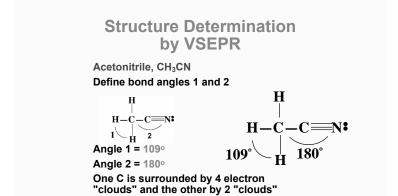
1. Draw electron dot structure

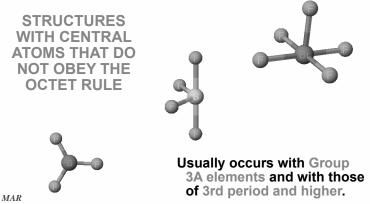
2. Define bond angles 1 and 2

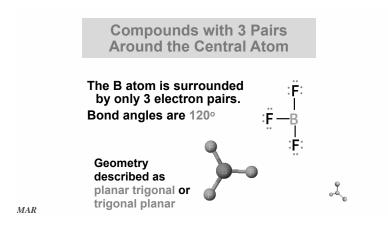
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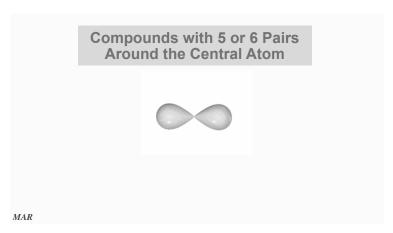
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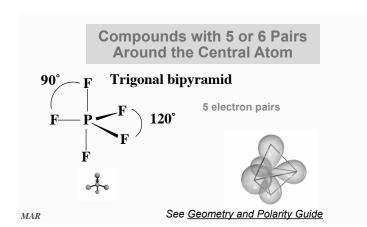
Structure Determination by VSEPR Methanol, CH₃OH Define bond angles 1 and 2 Angle 1 = 109° Angle 2 = 109° In both cases the atom is surrounded by 4 electron pairs.

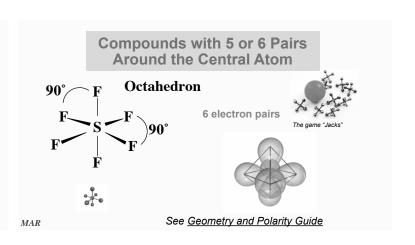


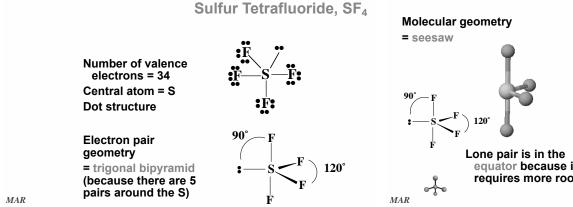


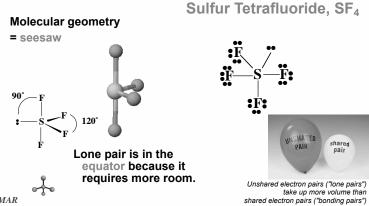


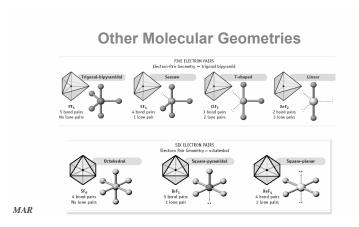


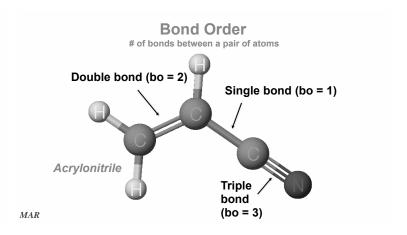


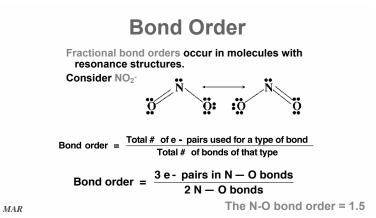




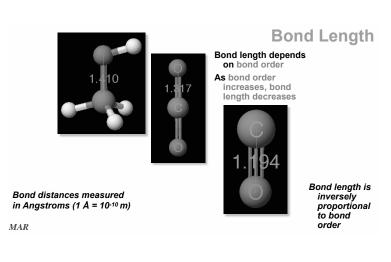


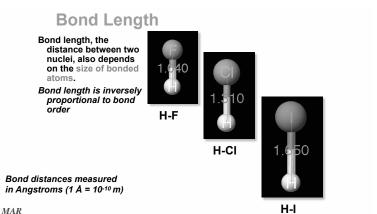


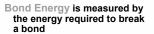




Bond Order Bond order is related to two important bond properties: bond length bond energy 745 kJ **Bond length** Bond energy is is inversely proportional proportional to bond order to bond order Bond lengths measured in pm (1 pm = 10^{-12} m) or Angstroms (1 $Å = 10^{-10} \, \text{m}$) Bond energies measured in kJ (1 kJ = 10^3 J) MAR





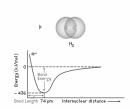


The GREATER the number of bonds (bond order) the LARGER the bond energy and the SHORTER the bond.

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Average Bond Enthalpies (kJ/mol)							
Single B	onds						
с-н	413	N-H	391	0-н	463	F-F	15
C-C	348	N-N	163	0-0	146		
C-N	293	N-O	201	O-F	190	CI-F	25
C-0	358	N-F	272	0-01	203	CI-CI	24
C-F	485	N-CI	200	0-1	234		
C-CI	328	N-Br	243			Br-F	23
C-Br	276			S-H	339	Br-CI	21
C-I	240	н-н	436	S-F	327	Br-Br	19
C-S	259	H-F	567	s-ci	253		
		H-CI	431	S-Br	218	1-C1	20
Si-H	323	H-Br	366	5-5	266	1-Br	17
Si-Si	226	H-I	299			1-1	15
Si-C	301						
Si-O	368						
Si-Cl	464						
Multiple	Bonds						
c=c	614	N=N	418	O+	495		
C = C	839	N=N	941				
C=N	615	N=O	607	s=0	523		
C=N	891			s-s	418		
C-0	799						
c=0	1072						

Bond Energy

Bond Energy $\circ = \circ$ 121 pm Bond order =2 498 kJ/mol

Using Bond Energies

Estimate the energy of the reaction:

H-H + CI-CI → 2 H-CI

Net energy = ΔH_{rxn} = energy required to break bonds - energy evolved when bonds formed

H-H = 436 kJ/molCI-CI = 243 kJ/molH-CI = 431 kJ/mol

 ΔH = bonds broker - bonds formed

Using Bond Energies

 ΔH = bonds broken bonds formed

Estimate the energy of the reaction: H-H + CI-CI ----> 2 H-CI

H-H = 436 kJ/molCI-CI = 243 kJ/molH-CI = 431 kJ/mol

H-Hcı—cı ΔH° = +679 kJ

"Bonds broken" or "Reactant bonds": H-H + CI-CI bond energies = 436 kJ + 243 kJ = 679 kJ

"Bonds formed" or "Product bonds": 2 mol H-Cl bond energies = 2 x 431 kJ = 862 kJ

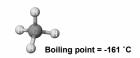
 ΔH = bonds broken - bonds formed

 $\Delta H = 679 \text{ kJ} - 862 \text{ kJ} = -183 \text{ kJ}$ MAR

exothermic!

Molecular Polarity

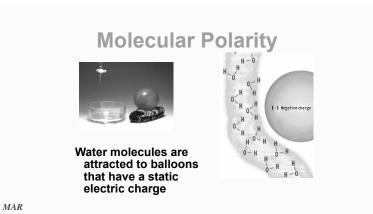






Why do ionic compounds dissolve in water?

Why do water and methane differ so much in their boiling points?



Bond Polarity



HCI is POLAR because it has a positive end and a negative end (dipoles).



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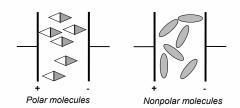
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CI has a greater share in bonding electrons than does H.

CI has slight negative charge $(-\delta)$ and H has slight positive charge $(+\delta)$

Bond Polarity

Dipole moment, μ , can measure dipole strength by placing molecules in electrical field. Polar molecules will align when the field is on. Nonpolar molecules will not.



+δ -δ H–**Ç**l:

Bond Polarity

Due to polarity, the H-Cl bond energy is GREATER than expected for a "pure" covalent bond.

BOND

ENERGY

"pure" bond real bond

339 kJ/mol calc'd 432 kJ/mol measured

Difference = 92 kJ. This difference is proportional to the difference in ELECTRONEGATIVITY, χ.

See <u>Polarity Guide</u>

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Electronegativity, χ

\(\chi\) is a measure of the ability of an atom in a molecule to attract electrons to itself.

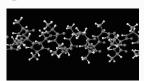


Electronegativities tend to increase up and to the right on the periodic table



Linus Pauling, 1901-1994





The only person to receive two unshared Nobel prizes (for Peace and Chemistry)

Chemistry areas: bonding, electronegativity, protein structure

A great Oregonian and a great Scientist

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Electronegativity, χ

si^{PS} Electro

F has maximum $\chi.$ Atom with lowest χ is the center atom in most molecules.

Relative values of χ determine BOND POLARITY (and point of attack on a molecule).

We are using "traditional" electronegativity values, but a new system has been introduced (January 2019)

Bond Polarity

Which bond is more polar (or DIPOLAR)?

 $\begin{array}{cccc} & & \text{O-H} & & \text{O-F} \\ \chi & & 3.5 \text{ - 2.1} & & 3.5 \text{ - 4.0} \\ \Delta \chi & & 1.4 & & 0.5 \end{array}$

.. OH is more polar than OF

O−H O−F -δ +δ +δ -δ

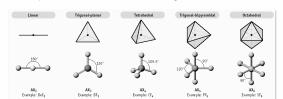
and polarity is "reversed"

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Molecular Polarity

Molecules will be polar if

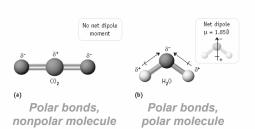
- a) bonds are polar AND
- b) the molecule is NOT "symmetric"



All above are symmetric and NOT polar (nonpolar)

Polar or Nonpolar?

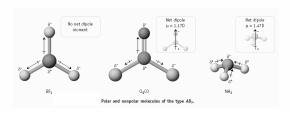
Compare CO₂ and H₂O. Which one is polar?



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Polar or Nonpolar?

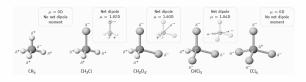
Consider AB₃ molecules: BF₃, Cl₂CO, and NH₃.



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CH₄ through CCl₄ Polarity



Methane (CH₄) and carbon tetrachloride (CCl₄) are symmetrical and NOT polar.

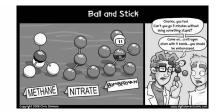
All other compounds asymmetrical and polar.

More on Molecular Polarity

All of these molecules are nonpolar due to their symmetry.

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End of **Chapter 7**



See:

- · Chapter Seven Study Guide
- Chapter Seven Concept Guide
- · Important Equations (following this slide)
- · End of Chapter Problems (following this slide)

Important Equations, Constants, and Handouts from this Chapter:

- know how to determine if ionic, covalent or metallic bonds are present
- · ionic bond strength determined by Coulomb's Law
- # valence electrons = group number (US periodic bonding pairs, lone pairs, table!)
- know the relationship between bond order, bond length and bond energy
- see Geometry and Polarity Guide and Bond Enthalpies and Electronegativities (handouts)

Formal Charge = Group Number bonds - lone pair electrons FC = GN - bonds - Ipe

 ΔH_{rxn} = bonds broken bonds formed

Lewis Structures / VSEPR: valence electrons, core electrons, total electrons, sigma bond, pi bond, VSEPR name (EPG & MG), formal charge, bond angles, polar, nonpolar, paramagnetic, diamagnetic, resonance structures, isomers

bond order (resonance) = $\frac{\# of e^{-} pairs used for a type of bond}{\# of bonds of that type}$

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End of Chapter Problems: Test Yourself

See practice problem set #1 and self quizzes for

- Lewis Structure / VSEPR examples and practice

 1. Which of the following elements are capable of forming compounds in which the indicated atom has more than four valence electron pairs? N, As, C, O, Br, Be, S, Se
- Which compound in each of the following pairs should require the higher temperature to melt?

 a. KBr or CsBr
 - h SrS or CaS
- c. LiF or BeO

 Describe the EPG and MG around N in NH₂Cl.
- Describe the EPG and MG around Cl in CIF₅.

 Describe the EPG and MG around Te in TeF₄.
- Which molecules are polar and which are nonpolar? H₂O, NH₃, CO₂, CIF,
- Give the bond order for each bond in the following molecules or ions:
- CH₂O, CO₂, NO₂-1, CH₄

 Oxygen diffuoride is quite reactive with water, giving oxygen and HF: OF₂(g) + H₂O(g) \rightarrow O₂(g) + 2 HF(g) $\stackrel{\triangle}{\Delta}$ H°_{con} = -318 kJ Using bond energies, calculate the bond dissociation energy of the O-F bond in OF₂.

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End of Chapter Problems: Answers

- As, Br, S and Se a. KBr b. CaS c. BeO tetrahedral and trigonal pyramid

- tenaneura and ingonar pyramid cotahedral and square pyramid trigonal bipyramid and seesaw polar: H₂O, NH₃, CIF nonpolar: CO₂, CCl₄ CH₂O (2xBO=1 (C-H), 1xBO=2 (C=O)), CO₂ (2xBO=2 (C-O)), NO₂*1 (2xBO=2 (N-O)), CH₄ (4xBO=1 (C-H))
- 8. D(O-F) = 195 kJ/mol

See practice problem set #1 and self quizzes for Lewis Structure / VSEPR examples and practice